Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

July 1, 2004 – September 30, 2004

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," during the time-period July 1, 2004 through September 30, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE), and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. Oxidized mercury is removed in the wet FGD absorbers and collected with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale to provide engineering data for future full-scale designs. The pilot-scale tests will continue for 14 months or longer at each of two sites to provide longer-term catalyst life data.

This is the twelfth full reporting period for the subject Cooperative Agreement. During this period, operation of the first pilot unit at the GRE Coal Creek site was concluded. Testing efforts included end-of-test pilot wet FGD tests treating flue gas from downstream of two of the four catalysts, and attempts to thermally regenerate, in situ, the mercury oxidation activity of three of the four catalysts. The pilot wet FGD tests were conducted as part of NETL project DE-FC26-04NT41992, and are reported in the Quarterly Technical Progress Report for that project. Also during the quarter, the results of Ontario Hydro relative accuracy tests conducted in June became available.

For the second pilot unit at CPS' Spruce Plant, the catalyst pilot unit continued in operation throughout the quarter. One catalyst activity measurement trip was conducted, in August, and the pilot wet FGD system mentioned above was shipped to the site.

This technical progress report details available results from these efforts at both sites.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period July 1, 2004 through September 30, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE) and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. The oxidizing species are already present in the flue gas, and may include chlorine, hydrochloric acid (HCl) and/or other species. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with and/or adsorbs on the byproducts from the FGD system. The objective of this project is to test previously identified catalyst materials at pilot scale to provide engineering data for future full-scale designs. The pilot-scale tests will continue for 14 months or longer at each of two sites to provide longer-term catalyst life data. After successful completion of the project, it is expected that sufficient full-scale test data will be available to design and implement demonstration-scale installations of the catalytic mercury oxidation technology.

The two utility team members are providing co-funding, technical input, and host sites for testing. GRE is providing the first test site at their Coal Creek Station (CCS), which fires a North Dakota lignite, and CPS is providing the second site at their J.K. Spruce Plant, which fires a Powder River Basin (PRB) subbituminous coal. These two host sites each have existing wet FGD systems downstream of high-efficiency particulate control devices, an ESP at CCS and a reverse-gas fabric filter (baghouse) at Spruce**.**

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, July 1, 2004 through September 30, 2004, is the twelfth full technical progress reporting period for the project. During this period, operation of the first pilot unit at the GRE Coal Creek site was concluded. Testing during the quarter included end-of-test pilot wet FGD tests conducted with flue gas from downstream of two of the four catalysts, and attempts to thermally regenerate, in situ, the mercury oxidation activity of three of the four catalysts. The pilot wet FGD tests were conducted as part of NETL project DE-FC26-04NT41992, and are reported in the Quarterly Technical Progress Report for that project. Also during the quarter, the results of Ontario Hydro relative accuracy tests conducted in June became available. For the second pilot unit at CPS' Spruce Plant, the catalyst pilot unit continued in operation throughout the quarter. One catalyst activity measurement trip was conducted, in August, and the pilot wet FGD system mentioned above was shipped to the site.

The pilot unit at CCS is installed at the outlet of an induced draft fan and downstream of the cold-side electrostatic precipitator on Unit 1. An SCR catalyst and a palladium-based catalyst (Pd #1) were placed in operation October 3, 2002. A subbituminous ash-based catalyst, SBA #5, was placed in service the first week in December 2003. The fourth, Carbon #6 (C #6) catalyst was installed and placed in service on June 5, 2003. Sonic horns were also installed and placed in service on June 5 as a means of limiting fly ash buildup on catalyst surfaces.

The final catalyst activity measurement trip conducted in June, 2004 showed 79% Hg^0 oxidation for the C #6 catalyst, with nearly 13 months of operation in flue gas, and about 67% oxidation for the Pd #1 catalyst after more than 20 months of operation. Significantly lower activity (<30% oxidation) was measured for the SCR and SBA #5 catalysts, after 20 and 18 months of operation, respectively.

Results of in situ thermal catalyst regeneration tests conducted in July showed that the Pd #1 catalyst improved from 67% elemental oxidation across the catalyst in June to 88% after regeneration, while the SCR catalyst improved from 26% in June to 46% after regeneration. The C#6 regeneration test was conducted in September, and showed no improvement in activity after thermal regeneration. No attempt was made to regenerate the SBA #5 catalyst, which was found to be plugged with fly ash buildup at the end of the test in June. After the C #6 regeneration test was concluded, the oxidation catalyst pilot unit was removed from the CCS site and shipped to TXU Power's Monticello Steam Electric Station in Mount Pleasant, Texas, for catalyst testing as part of NETL project DE-FC26-04NT41992.

At CPS' Spruce Plant, catalyst activity results were measured during the month of August. These measurements showed that the fabric filter outlet flue gas mercury content is still highly oxidized (~90%). The low inlet elemental mercury concentrations to the pilot unit (1-2 $\mu g/Nm^3$) make it difficult to quantify catalyst oxidation activity. To improve the accuracy of the mercury oxidation measurements, for this trip a new mercury SCEM with a more sensitive atomic absorption detector was used at the catalyst outlet location, to improve the ability to measure low elemental mercury concentrations. The catalyst activity results from this trip indicate 80-90%

elemental mercury oxidation across each of the four catalysts. These results show somewhat lower oxidation percentages across the catalysts than were measured in May (>90%). However, the inlet elemental mercury concentrations to the pilot unit were higher in May. The resulting catalyst outlet elemental mercury concentrations were similar in May and in August, at approximately 0.1 to 0.2 $\mu g/Nm^3$, representing 98 to 99% overall mercury oxidation in the catalyst outlet flue gas.

No subcontracts were issued during the current reporting period.

Problems Encountered

There were no significant new problems encountered during the reporting period, other than the technical issues described in Section 4 of this report and mentioned above.

Plans for Next Reporting Period

During the next reporting period (October 1 through December 31, 2004), there will be no further pilot-scale tests conducted at Coal Creek as part of this project. Only data reduction and reporting activities remain. The pilot unit has been removed from CCS and shipped to TXU's Monticello Station as part of project DE-FC26-04NT41992.

Operation of a second oxidation catalyst pilot unit, at CPS' Spruce Plant, will continue with all four catalysts installed until the end of calendar year 2004, and catalyst activity will be evaluated for elemental mercury oxidation activity through routine (~bimonthly) evaluation trips. Ontario Hydro relative accuracy tests for the mercury SCEM will be conducted during the quarter. Also, pilot wet FGD tests will be conducted downstream of each of the four catalysts during the quarter, but as part of the 41992 project.

Prospects for Future Progress

During the subsequent reporting period (January 1 through March 31, 2005), no testing is scheduled at either of the two sites, as both pilot units will have been shut down and moved to new sites as part of the 41992 project. The only remaining project efforts will be data reduction and reporting.

EXPERIMENTAL

The work described in this technical progress report was conducted using two different experimental apparatuses. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated) located at GRE's CCS Station in North Dakota. A nearly identical pilot unit is located at CPS' Spruce Plant. Each pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device and upstream of its FGD system. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports[1,2, 3, 4].

The activity of these catalysts is being determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily being conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[5]. Periodically, the analyzer results are being verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The second experimental apparatus is a bench-scale test unit that is used to evaluate the activity of candidate catalyst cores under simulated flue gas conditions. However, no bench-scale tests were conducted during the current quarter. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports[3, 4].

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, July 1, 2004 through September 30, 2004. The technical results presented include a discussion of the data from the first pilot unit at GRE's CCS and the second pilot unit at CPS' Spruce Plant.

Pilot Unit Operation at CCS

Background

As described in previous quarterly reports, the first pilot unit started up at CCS with the SCR and Pd #1 catalysts the first week of October 2002. The other two catalysts (SBA #5 and C #6) were not yet available. Initial catalyst activity measurements, obtained by mercury SCEM, showed 95% oxidation of elemental mercury across the Pd#1 catalyst, while the SCR catalyst showed 67% oxidation. Throughout this report, elemental mercury oxidation percentages across catalysts are reported based on the measured decrease in elemental mercury concentration across the catalyst, and do not just reflect the total flue gas mercury oxidation percentage at the catalyst outlet.

In December 2002, the third catalyst, SBA #5, was installed. Measurement results showed a marked decrease in activity for both the Pd #1 and SCR catalysts. Follow-up testing in January determined that the catalyst surfaces were becoming plugged due to buildup of fly ash in the horizontal-gas-flow catalyst cells, in spite of the catalysts being installed downstream of a high-efficiency ESP. This was confirmed by pressure drop increases across the catalysts and by opening and physically inspecting the catalyst chambers to observe and clean out the fly ash buildup.

It appeared that mechanical catalyst cleaning would be needed on the pilot unit for the horizontal-gas-flow catalysts. Both air soot blowers and sonic horns were considered. It was decided that a sonic horn would be the easiest field retrofit and would offer a good probability of success. A small, 17-inch horn produced by Analytec Corporation of Pagosa Springs, Colorado was selected for testing. During the last week of March 2003, the sonic horn was installed on the Pd #1 catalyst box to provide occasional pulses of acoustic energy to the catalyst to dislodge accumulated particulate matter. The horn was installed on the top wall of the catalyst housing inlet transition, approximately 1.5 feet upstream of the first catalyst module. The horn sounds for 10 seconds every half hour. When the sonic horn was installed, the catalyst housing was opened and the Pd #1 catalyst modules were cleaned.

The horn proved to be effective at controlling pressure drop across the Pd #1 catalyst. A catalyst activity measurement trip was conducted one month later. While the Pd #1 results were confounded by apparent mercury adsorption across the catalyst (i.e., a portion of the drop in elemental mercury concentration across the Pd #1 could be due to adsorption rather than oxidation) they otherwise showed high (~90%) elemental mercury oxidation across the catalyst. Based on the relatively high activity and low pressure drop values for Pd #1, sonic horns were installed on the other three boxes the first week of June 2003.

With the horns in service, the pressure drops across three of the four catalysts appear to have remained low. However, since approximately January 2004, the signals for pressure drop across all four catalyst boxes became very noisy.

The SBA #5 pressure drop increased over time, and averaged between 3 and 5 in. H_2O during the final quarter of pilot unit operation. This is more than 10 times the initial pressure drop on June 5, 2003. It appears that there is a particle-to-particle attraction between the fly ash in the flue gas treated and the fly ash imbedded in the catalysts. This catalyst type is of lesser interest for future commercial applications, so regardless of the cause, the pressure drop increase across this catalyst chamber is not of great concern. The average pressure drop across the other catalysts remained below 1 in. H_2O, indicating the effectiveness of the sonic horn in preventing fly ash buildup.

The final catalyst activity measurement trip was conducted in June, 2004. Measurements by Hg SCEM showed 79% Hg^0 oxidation for the C #6 catalyst, with nearly 13 months of operation in flue gas, and about 67% oxidation for the Pd #1 catalyst after more than 20 months of operation. Significantly lower activity was measured for the SCR catalyst, with 26% oxidation measured after 20 months of operation and for the SBA #5 catalyst, with only 12% oxidation measured after 18 months of operation.

Results From the Current Quarter

In June 2004, Ontario Hydro (OH) relative accuracy tests were conducted across the Pd #1, SCR and C #6 catalysts during simultaneous measurements with the mercury SCEM. The SCEM results were reported in the previous Quarterly Technical Progress Report, but Ontario Hydro results were not yet available. These results are now available and are reported below in Table 1. Ontario Hydro measurements were made across each catalyst module; the different catalysts were tested sequentially using two gas testing setups located at the inlet and outlet of the respective catalyst boxes.

The results for the Pd #1 catalyst show reasonably good agreement, with the SCEM results showing a small, but consistent negative bias compared to the Ontario Hydro results (-6 to -12% for the total and elemental Hg measurements). This error could have been introduced by a single error such as a 5 to 10% calibration error in the mass flow meter used in the SCEM, or by the cumulative effects of several small errors.

For the other two catalysts, the total mercury concentration measurements agreed very well, with relative accuracy percentages ranging from –5.2% to +8.8%, as did the catalyst inlet speciation. The catalyst outlet mercury speciation results did not agree as well. As was seen in the last set of OH relative accuracy tests at CCS in July 2003, the OH results show much lower catalyst outlet elemental Hg concentrations than the SCEM results for these two catalysts. In both the July 2003 and June 2004 data, the outlet elemental Hg concentrations from the Pd #1 catalyst agreed reasonably well between the two methods.

As was discussed when the July 2003 OH results from CCS were reported, we believe the SCEM results are a better indicator of catalyst performance for the SCR and C #6 catalysts, but have no clear explanation why this bias exists. The most convincing evidence that the bias exists with

the OH method rather than the SCEM data is seen in comparing the OH results from the three sets of OH measurements at CCS. The first set, in October 2002, showed 69% oxidation of

Table 1. June 2004 Ontario Hydro Relative Accuracy Results for CCS Pilot (compared to Hg SCEM results)

	Total	Elemental	Oxidized
Pd #1, June 26, 2004			
Catalyst Inlet – OH, μg/Nm^3*	14.7	10.3	4.33
Catalyst Inlet - SCEM, μg/Nm^3	13.2	9.53	3.68
Relative Accuracy, %	-10.0%	-7.9%	-15.0%
Catalyst Outlet - OH, μg/Nm^3	14.59	3.32	11.27
Catalyst Outlet - SCEM, μg/Nm^3	12.78	3.11	9.67
Relative Accuracy, %	-12.4%	-6.2%	-14.2%
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	68	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	67	-
SCR, June 27, 2004			
Catalyst Inlet - OH, μg/Nm^3	15.2	11.3	3.86
Catalyst Inlet - SCEM, μg/Nm^3	15.4	11.0	4.38
Relative Accuracy, %	1.4%	-2.7%	13.5%
Catalyst Outlet - OH, μg/Nm^3	14.1	3.41	10.6
Catalyst Outlet - SCEM, μg/Nm^3	15.3	8.14	7.15
Relative Accuracy, %	8.8%	138.9%	-32.8%
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	70	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	26	-
C #6, June 28, 2004			
Catalyst Inlet - OH, μg/Nm^3	15.8	12.1	3.68
Catalyst Inlet - SCEM, μg/Nm^3	15.0	9.89	5.12
Relative Accuracy, %	-5.2%	-18.5%	39.0%
Catalyst Outlet - OH, μg/Nm^3	14.3	0.75	13.6
Catalyst Outlet - SCEM, μg/Nm^3	14.6	2.09	12.5
Relative Accuracy, %	2.1%	178.5%	-7.7%
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	94	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	79	-

*Note – All concentrations corrected to 3% O_2, dry basis; 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

elemental mercury across the SCR catalyst, which had only been in service for only two weeks. The second measurement, in July 2003, showed 92% oxidation across the catalyst, which is an unlikely increase after 9 months in flue gas service. The third measurement, in June 2004, showed 70% oxidation across the SCR catalyst, still slightly higher than what was measured for the fresh catalyst.

In July, attempts were made to thermally regenerate the SCR and Pd #1 catalysts in situ. The attempted regeneration of the C #6 catalyst was delayed until September due to equipment and personnel scheduling issues. Each thermal regeneration was conducted by replacing the sonic

horn on the inlet of the catalyst chamber with a 36-KW duct heater. The inlet flue gas flow to the compartment being regenerated was closed off, and an air supply was connected to the duct heater. The duct heater outlet air temperature was controlled to 600°F. This was set as the upper limit for the regeneration air temperature based on the temperature rating for the gasket material used to seal the compartment access covers. The regeneration air flow was limited by the heater capacity at about 280 acfm as measured downstream of the catalyst, at a maximum temperature of about 410 to 420°F. This downstream temperature was also a constraint on the thermal regeneration, as the Teflon seats in the downstream catalyst chamber flow control valves could not exceed 450°F. The difference between the inlet air temperature of 600°F and the maximum outlet temperature achieved, of 420°F, was due to heat losses through catalyst chamber walls.

The hot air flow was allowed to continue through the afternoon that the test started and overnight. After heating each catalyst with 600°F air overnight, it was placed back in flue gas service and catalyst activity was measured by SCEM to determine if the elemental mercury oxidation activity increased.

The results from these tests are summarized in Table 2. The results in Table 2 show that the activities of the Pd #1 and SCR catalysts improved measurably after the thermal regeneration. The Pd #1 activity improved to near the activity of the fresh catalyst (88% vs. 95%) while the SCR catalyst improved to about two-thirds of its original activity (46% vs. 67%). However, the C #6 catalyst showed no measurable improvement in activity after the thermal regeneration. It is possible that the species which causes activity loss by the C #6 catalyst is more strongly adsorbed to the carbon-based catalyst than to the other, metal based catalysts. After the catalysts are recovered from the pilot unit, samples of the C #6 catalyst will be thermally regenerated in the lab to see if greater improvements can be realized with higher regeneration temperatures.

Table 2. Results of CCS Catalyst Regeneration Tests

Catalyst	Elemental Mercury Oxidation Across Catalyst, %			
	Fresh Catalyst (date)	End of Test (6/04)	Prior to Regeneration (date)	After Regeneration (date)
Pd #1	95 (10/02)	67	79 (7/04)	88 (7/04)
SCR	67 (10/02)	26	25 (7/04)	46 (7/04)
C #6	98 (6/03)	79	53* (9/04)	48(9/04)

*Estimated because there was not a catalyst inlet Hg^0 concentration measurement made near the time period the catalyst outlet was measured; catalyst inlet Hg^0 concentration was estimated from total Hg and assumed 34% oxidation.

Some of the results shown in Table 2 warrant further discussion. One is that the observed activity of the Pd #1 catalyst was measured to be higher prior to regeneration in late July than it had been at the end of the long-term catalyst pilot evaluation in June. There is a probable explanation for this observation. The Pd #1 catalyst material had been observed to readily regenerate in the past, during the Mega-PRDA project (DE-AC22-95PC95260), often improving in performance just by removing the catalyst from flue gas exposure. During the time that elapsed between when the long-term test ended and the regeneration tests were conducted, the pilot unit was shut down several times, and ambient air was allowed to enter the catalyst chambers while new ports were welded onto the catalyst outlet duct to accommodate pilot wet FGD tests. It is likely that the

species that adversely affect the activity of the Pd #1 desorbed to some extent just by ceasing flue gas flow through the catalyst several times and exposing the catalyst to ambient air.

As noted in Table 2, an estimate was required for the oxidation across the C #6 catalyst prior to regeneration because there was not a catalyst inlet elemental mercury concentration measurement near the time the outlet was measured. A review of the data showed that the inlet total mercury concentration had changed since the time the catalyst inlet elemental mercury concentration was measured. Consequently, the catalyst inlet elemental mercury concentration at the time the outlet was measured was estimated from the inlet total measured near that time multiplied by an interpolated inlet oxidation percentage (34%). This value was interpolated between the oxidation measured previously (36%) and after the regeneration was completed (32%).

Assuming this estimate for the C #6 catalyst is reasonably accurate, the activity prior to regeneration (53%) was lower than the end of test value from June (79%). During the three months that elapsed between the end of the long-term test and when this regeneration test was conducted, the pilot unit was shut down and restarted a number of times, and operated for several periods with flue gas flow through the catalysts but without the sonic horns in service. It is possible that the C #6 catalyst became partially plugged with fly ash over this period. When the catalysts are recovered from the pilot unit in late October or early November, this catalyst will be inspected to observe whether there is significant fly ash buildup.

The most important note about these regeneration test results is that they were intended to be "proof of concept" tests to determine if the catalysts could be thermally regenerated. The conditions were not optimized to ensure the effectiveness of the thermal regeneration, though. For example, it is known that the air entering the catalyst chamber was at 600^{o}F, and that the air in the 6-in. discharge piping from the catalyst chamber reached a maximum of 410 to 420^{o}F, but it is not known what was the actual maximum temperature achieved at the catalyst surfaces. Also, the regeneration air flow of approximately 280 acfm was much lower than the normal flue gas flow through these catalysts (1500 to 2000 acfm), and the regeneration air flow was introduced from the top surface of the catalyst chamber inlet transition duct rather than through the centered inlet duct run. Because of this, it is possible that only portions of the catalysts saw appreciable regeneration air flow. In future regeneration tests, it is recommended that a larger heater be used, to allow a greater air flow that will better distribute across the catalyst cross section, and that thermocouples be retrofitted to the catalyst chamber to allow temperatures to be monitored across the cross section of the catalyst outlet plane.

Pilot Unit Operation at Spruce Plant

Background

The pilot unit was started up at Spruce Plant in late August 2003 and operated with the Pd #1 and Au catalysts installed for most of the month of September. The host unit came off line for a fall outage the evening of September 26, and the outage continued until October 27. The two remaining catalysts (SCR and C #6) were installed in the pilot unit and the pilot unit was

restarted on November 13. The unit has operated continuously with all four catalysts on line since then.

Pilot unit inlet and catalyst outlet mercury concentration data were collected at Spruce the week of December 8. SCEM relative accuracy tests by the Ontario Hydro Method were conducted at the same time. The week of January 5, two SCEMs were taken to the site and used to measure flue gas total mercury and elemental mercury concentrations at the fabric filter inlet and outlet, and at the wet FGD outlet locations on the host unit. These measurements were made to develop a baseline characterization of host unit flue gas mercury conditions prior to rebagging the fabric filter with new bags. The rebagging began on January 12. Routine catalyst activity measurements by Hg SCEM were made on February 13, after 11 of the 14 compartments in the west fabric filter (directly upstream of the catalyst pilot unit) had been rebagged. The rebagging was completed at the end of February. These results have all been reported previously. During the current quarter, catalyst activity measurements were made across all four catalysts by mercury SCEM.

Catalyst Pressure Drop Results

The pressure drop across the four catalyst chambers at Spruce remained nearly constant between 0.2 and 0.3 in H_2O during the current quarter. It does not appear that sonic horns will be required to prevent fly ash buildup, most likely because a high-efficiency reverse-gas fabric filter is used for particulate control at this site. The use of a fabric filter results in a low dust loading in the pilot unit inlet flue gas, and a dust loading that has less residual electrostatic charge than would flue gas downstream of an ESP.

Catalyst Activity Results

One set of catalyst measurement trip results are presented in this report, from August 2004. These results are shown in Table 3.

Table 3. August Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Total Hg (mg/Nm^3, corrected to 3% O_2)*	Elemental Hg (mg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Pd #1 Inlet	9.66	1.25	-	-	87
Pd #1 Outlet	9.81	0.21	0	84	98
C #6 Inlet	11.3	1.25	-	-	89
C #6 Outlet	9.27	0.19	18	85	98
Au Inlet	12.4	1.25	-	-	90
Au Outlet	13.1	0.25	0	80	98
SCR Catalyst Inlet	12.4	1.25	-	-	90
SCR Catalyst Outlet	13.1	0.17	0	87	99

*Note: 1.00 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

As has been previously reported, the measurements at the pilot unit inlet showed high mercury oxidation percentages, with SCEM measurements showing 87% to 90% oxidized rather than the expected 20 to 30% oxidized mercury typical of PRB flue gases. This effect appears to be an influence of the fabric filter used for particulate control at Spruce. The fabric filter operates at a low air-to-cloth ratio (less than 1.5 acfm/ft^2) and at flue gas temperatures below 300^oF. The baghouse outlet elemental mercury concentrations averaged 1.25 $\mu g/Nm^3$, which is not at high as would be desired from the standpoint of being able to measure oxidation catalyst performance.

Measurement of catalyst activity at Spruce is difficult for two reasons. One is that because of mercury oxidation and capture across the fabric filter, the elemental mercury concentrations at the oxidation catalyst pilot unit are relatively low, typically 1 to 3 $\mu g/Nm^3$ as mentioned above. This means that for well performing catalysts, the catalyst outlet elemental mercury concentrations are considerably under 1 $\mu g/Nm^3$, a low concentration that is difficult to measure accurately with the Hg SCEM (or by any other method). The second difficulty is that the pilot inlet total and elemental mercury concentrations can change significantly throughout the day, perhaps being impacted by factors such as fabric filter pressure drop and compartment cleaning cycles. A single Hg SCEM was used to quantify catalyst performance during this trip, and had to cycle between the pilot inlet flue gas sample and the catalyst chamber outlet samples, so inlet concentration variations could have markedly impacted observed mercury adsorption and elemental mercury oxidation percentages.

Because of these difficulties in measuring catalyst performance, two mercury SCEMs were used during the previously reported May trip, one dedicated to measuring inlet mercury concentrations while the other cycled through the four catalyst chamber outlets. However, due to a heavy field workload in August, only one analyzer was available for the current trip. During both the May and August trips, URS' newest, highest resolution analyzer was used for measuring the catalyst outlets, and increased measurement cycle times were employed so that the amount of mercury captured on the analyzer gold trap was above the low instrument calibration standard.

It appears that all of the catalysts are performing well. In August, each measured greater than 80% oxidation of elemental mercury. While this is down somewhat from what was measured in May (when all were measured at greater than 90% oxidation), it should be noted that the catalyst inlet elemental mercury concentration was considerably lower in August than in May, with an average value of 1.25 $\mu g/Nm^3$ measured in August and values ranging from 2 to 3 $\mu g/Nm^3$ being measured in May. For both measurement trips, the catalyst outlet elemental mercury concentrations were very similar, all in the range of 0.1 to 0.2 $\mu g/Nm^3$ corrected to 3% O_2 (~0.1 to 0.2 $lb/10^{12}$ Btu heat input). It may be that these outlet concentrations represent the lower limit for the ability to measure low elemental mercury concentrations, so the observed elemental mercury percentage oxidation across the catalysts subsequently becomes a function of the inlet concentration.

Only one catalyst, the C #6 catalyst, appeared to be adsorbing mercury in significant quantities in August. It is not clear why this would be occurring, because during the May measurements this catalyst appeared to be at adsorption equilibrium. This suggests that some change occurred that affected the equilibrium between the catalyst surface and mercury present in the flue gas.

All of the catalyst activity results from Spruce since September 2003 are plotted in Figure 1. The early catalyst activity results show quite a bit of variability over time, and during some measurement periods the mercury oxidation percentages were much lower than expected. The most recent data, from the May and August measurement trips, are believed to be the most reliable and show that all four catalysts are achieving greater than 80% oxidation of the inlet elemental mercury. The next measurement trip is scheduled for late October, and will provide an opportunity to see whether the high activity results measured in May and August will be repeated.

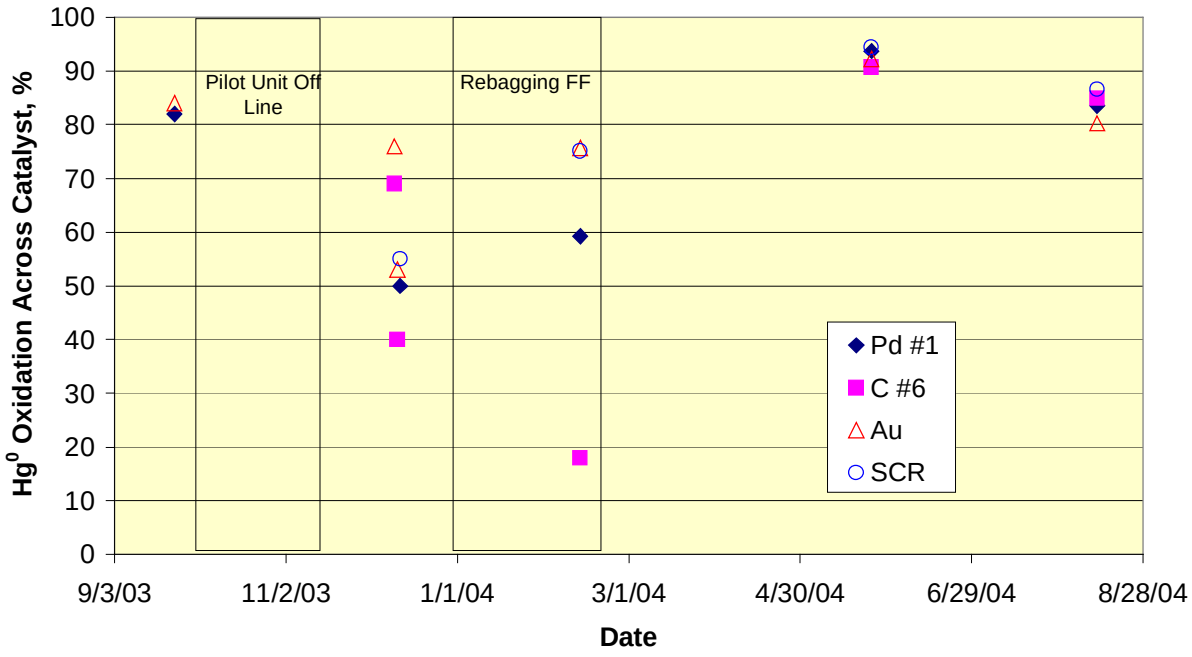

Figure 1. Catalyst Activity Versus Time in Service at Spruce Plant

Laboratory Evaluation of Candidate Catalysts

No laboratory evaluations were conducted during the current quarter.

CONCLUSION

Because of the observed ash accumulation on the catalysts at CCS, provisions had to be made to keep catalyst surfaces cleaner. Sonic horns are commonly used to clean catalysts on line in utility SCR applications for NO_X control, and appear to be similarly effective in this application (lower dust loading but horizontal gas flow). In 13 months of operation, the horns were apparently effective at limiting fly ash buildup in three of the four catalysts. For the fourth catalyst, SBA #5, it appears that the sonic energy from the horn was not sufficient to prevent fly ash accumulation (and loss of activity), perhaps because of electrostatic attraction between the fly ash particles in the flue gas and catalyst.

Catalyst activity measurements in June, 2004 indicated that the horns were also been effective in maintaining catalyst activity for two more active catalyst materials. After 20+ months of operation, the Pd #1 catalyst saw some long-term loss in activity for elemental mercury oxidation, from 95% to between 65 and 70%. After nearly 13 months of operation, the C #6 catalyst dropped from greater than 95% to between 75 and 80%. The SCR catalyst saw a more significant loss, dropping from 67% to 26% oxidation over a 20+-month period (as measured by SCEM). The SBA #5 catalyst dropped from 75% oxidation to about 12% oxidation over an 18+-month period, although fly ash buildup contributed to that loss.

Catalyst regeneration tests conducted during the current reporting period showed that the activity of the Pd #1 and SCR catalysts could be markedly improved by thermal regeneration with 600^{o}F air, but the thermal regeneration was ineffective on the C #6 catalyst. This suggests that the loss of activity over time by these catalysts is due to adsorption of interfering species onto active catalyst sites, and that these species are readily desorbed from the metal-based catalysts but are more strongly adsorbed by the carbon-based catalyst. Previous EPRI testing has shown that thermal regeneration of activated carbon (mercury) sorbents is very material-specific and that some samples may require very high temperatures[8].

Ontario Hydro relative accuracy test results available this quarter from June 2004 tests show good agreement with the Hg SCEM for total mercury concentrations, and reasonably good agreement for mercury speciation at the catalyst inlets. However, the catalyst outlet results were mixed, with good agreement for the outlet of the Pd #1 catalyst, while the Ontario Hydro method showed considerably lower elemental mercury concentrations than the Hg SCEM at the SCR and C #6 catalyst outlets. A similar bias was seen for these catalysts during previous Ontario Hydro relative accuracy tests in July 2003. The project team feels the evidence points to the measurement bias being with the Ontario Hydro method rather than the Hg SCEM, although it is not clear what about these catalysts produces this bias.

At the Spruce site, the fabric filter upstream of the pilot unit has had two implications on the pilot testing. One is that is does not appear that sonic horns will be required to keep fly ash from accumulating within the catalyst cells. The other implication is that the fabric filter oxidizes a high percentage of the elemental mercury in the air heater outlet flue gas, so the inlet gas to the pilot unit contains relatively low elemental mercury concentrations (typically 1 to 3 $\mu g/Nm^3$). This makes evaluation of catalyst performance difficult, as it is difficult to quantify flue gas elemental mercury concentrations that are well below 1 $\mu g/Nm^3$.

Based on results from August, all four catalysts (Au, C #6, Pd #1 and SCR catalysts) are achieving greater than 80% elemental mercury oxidation in this PRB flue gas, and are lowering catalyst outlet elemental mercury concentrations to the detection limits of the Hg SCEM, in the range of 0.1 to 0.2 $\mu g/Nm^3$. During the upcoming quarter, site measurements will be conducted to determine whether these high catalyst activity results will be repeated.

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